

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
4 March 2004 (04.03.2004)

PCT

(10) International Publication Number
WO 2004/018094 A1

(51) International Patent Classification⁷: **B01J 23/745**,
C07C 1/04, C10G 2/00

(21) International Application Number:
PCT/EP2003/008770

(22) International Filing Date: 6 August 2003 (06.08.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/402,379 9 August 2002 (09.08.2002) US
02079413.7 24 October 2002 (24.10.2002) EP

(71) Applicant: **AKZO NOBEL N.V.** [NL/NL]; Velperweg 76,
NL-6824 BM Arnhem (NL).

(72) Inventors: **STAMIRES, Dennis**; 1300 Colony Plaza,
Newport Beach, CA 92660 (US). **SPEE, Marieke**,
Paulyne, Réate; Texel 95, NL-3524 AS Utrecht (NL).
LAHEIJ, Erik, Jeroen; Graaf Aelbrechtlaan 14, NL-1181
SW Amstelveen (NL). **O'CONNOR, Paul**; Hogebrinker-
weg 9, NL-3871 KM Hoevelaken (NL).

(74) Agent: **SCHALKWIJK, Pieter, Cornelis**; Akzo Nobel
N.V., Intellectual Property Department (Dept. AIP), P.O.
Box 9300, NL-6800 SB Arnhem (NL).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: FISCHER-TROPSCH PROCESS USING AN IRON-CONTAINING LAYERED MATERIAL

(57) Abstract: Method for performing a Fischer-Tropsch process using as a catalyst (precursor) an iron-containing layered material selected from the group consisting of layered materials in which iron is present in the layered structure as divalent and/or trivalent metal (group 1), iron-doped layered materials (group 2), calcined iron-doped layered materials (group 3), and calcined layered materials in which iron is present in the layered structure as divalent metal (group 4). The term "layered material" includes anionic clays, layered hydroxy salts, cationic clays, and cationic layered materials.

WO 2004/018094 A1

FISCHER-TROPSCH PROCESS USING AN IRON-CONTAINING LAYERED MATERIAL

The present invention relates to a Fischer-Tropsch process using an iron-
5 containing layered material.

As explained by M.E. Dry in *Catal. Lett.*, Vol. 7 (1990) 241-252, the most
suitable catalytic metals for Fisher Tropsch synthesis, i.e. the production of
hydrocarbons from CO and H₂, are Fe, Co, and Ru. Of these metals, iron is the
10 least expensive and has the highest selectivity to olefins.

In order to reach a satisfactory selectivity, iron-containing catalysts require a
certain level of basicity. This basicity is usually created by the addition of alkali.
Unfortunately, alkali is known to migrate over the catalyst surface, enhancing
iron sintering. Furthermore, alkali enhances carbon lay-down on the catalyst,
15 leading to deactivation of the catalyst.

Apart from carbon lay-down, also sulphur poisoning might cause deactivation.
Furthermore, as a result of diffusion resistance inside the iron particles, the
water vapour pressures inside these particles can be relatively high, leading to
sintering and/or oxidation of the inner core of the iron particles.

20 Shen et al. disclose the use of calcined and subsequently reduced Mg-Fe
anionic clay (*Catal. Today* 30 (1996) 77-82 / *J. Solid State Chem.* 128 (1997)
73-79) and Ni-Fe anionic clay (*Thermochimica Acta* 302 (1997)) in a Fischer-
Tropsch process.

25 The present invention provides a method for performing a Fischer-Tropsch
process using iron-containing layered materials which is simpler than the
method of Shen. It involves fewer reaction steps and/or uses a catalyst that is
easier to prepare.

30 The method according to the invention comprises the steps of:

- a) selecting a Fischer-Tropsch catalyst precursor,
- b) optionally reducing the Fischer-Tropsch catalyst precursor to form a Fischer-Tropsch catalyst, and
- c) performing a Fischer-Tropsch synthesis using the Fischer-Tropsch catalyst precursor according to step a) or the Fischer-Tropsch catalyst according to step b),

wherein the Fischer-Tropsch catalyst precursor comprises an iron-containing layered material selected from the group consisting of layered materials in which iron is present in the layered structure as divalent and/or trivalent metal (group 1), iron-doped layered materials (group 2), calcined iron-doped layered materials (group 3), and calcined layered materials in which iron is present in the layered structure as divalent metal (group 4).

The term "layered material" includes anionic clays, layered hydroxy salts, cationic clays, and cationic layered materials.

Iron-containing layered materials according to group 1 include layered materials in which iron is the divalent metal or at least one of the divalent metals present in the layered structure (group 1a) and layered materials in which iron is the trivalent metal or at least one of the trivalent metals present in the layered structure (group 1b). Group 1 also includes layered materials in which iron is present as both divalent and trivalent metal.

Iron-doped layered materials according to group 2 include layered materials wherein iron or an iron-containing compound is present in or on the layered structure as an additive (or: dopant). It also includes layered materials in which iron is both present as dopant and as divalent and/or trivalent metal in the layered structure.

The term "calcined iron-doped layered materials" (group 3) refers to iron-doped layered materials according to group 2 that have been calcined. The term "calcined layered materials in which iron is present in the layered structure as

divalent metal" (group 4) refers to layered materials according to group 1a that have been calcined.

Calcination of group 1a and 2 layered materials is generally performed at temperatures in the range 200-1200°C under oxygen-containing or inert (e.g.
5 N₂, Ar, He) atmosphere.

It has now been found, in contrast to the teaching of Shen et al., that iron-containing layered materials do not have to be calcined prior to use in Fischer-Tropsch synthesis, but that they can be used directly, optionally after a
10 reduction step. The absence of a calcination step makes the process simpler and economically more attractive.

Furthermore, iron-doped layered materials (groups 2 and 3) have the additional advantage that they can be easily prepared and that the iron-content can be
15 easily adjusted to the desired value, because they can be prepared by impregnating an existing layered material with an iron-containing compound.

On the other hand, they can also be obtained by preparing the layered material in the presence of the additive. The latter method generally results in a more homogeneous distribution of the iron-containing compound throughout the
20 layered material.

Iron-doped layered materials generally comprise 1-35 wt%, preferably 5-20 wt%, more preferably 10 - 15 wt% of iron, calculated as Fe₂O₃ and based on the weight of the iron-doped layered material.

25 It is further noted that, as a result of its lower valence, the iron in group 1a layered materials is easier to reduce than the iron in group 1b layered materials, thereby requiring a lower reduction temperature and/or shorter reduction time.

Anionic clays

30 Anionic clays have a crystal structure consisting of positively charged layers built up of specific combinations of divalent and trivalent metal hydroxides

between which there are anions and water molecules. Hydrotalcite is an example of a naturally occurring anionic clay in which the trivalent metal is aluminium, the divalent metal is magnesium, and the predominant anion is carbonate; meixnerite is an anionic clay in which the trivalent metal is aluminium, the divalent metal is magnesium, and the predominant anion is hydroxyl.

It should be noted that a variety of terms are used to describe the material that is referred to in this specification as an anionic clay. Hydrotalcite-like and layered double hydroxide are interchangeably used by those skilled in the art. In this specification we refer to these materials as anionic clays, comprising within that term hydrotalcite-like and layered double hydroxide materials.

Anionic clays in which iron is the divalent metal or at least one of the divalent metals present in the anionic clay structure (according to group 1a) include Al^{3+} - Fe^{2+} anionic clay, B^{3+} - Fe^{2+} anionic clay, Ga^{3+} - Fe^{2+} anionic clay, In^{3+} - Fe^{2+} anionic clay, Bi^{3+} - Fe^{2+} anionic clay, Cr^{3+} - Fe^{2+} anionic clay, Sc^{3+} - Fe^{2+} anionic clay, La^{3+} - Fe^{2+} anionic clay, Co^{3+} - Fe^{2+} anionic clay, Ce^{3+} - Fe^{2+} anionic clay, Al^{3+} - $\text{Fe}^{2+}\text{Mg}^{2+}$ anionic clay, Al^{3+} - $\text{Fe}^{2+}\text{Zn}^{2+}$ anionic clay, Al^{3+} - $\text{Fe}^{2+}\text{Ni}^{2+}$ anionic clay, and Al^{3+} - $\text{Fe}^{2+}\text{Co}^{2+}$.

Anionic clays in which iron is the trivalent metal or at least one of the trivalent metals present in the anionic clay structure (according to group 1b) include Fe^{3+} - Mg^{2+} anionic clay, Fe^{3+} - Mn^{2+} anionic clay, Fe^{3+} - Ca^{2+} anionic clay, Fe^{3+} - Ba^{2+} anionic clay, Fe^{3+} - Zn^{2+} anionic clay, Fe^{3+} - Co^{2+} anionic clay, Fe^{3+} - Mo^{2+} anionic clay, Fe^{3+} - Ni^{2+} anionic clay, Fe^{3+} - Sr^{2+} anionic clay, Fe^{3+} - Cu^{2+} anionic clay, Fe^{3+} - $\text{Zn}^{2+}\text{Cu}^{2+}$, $\text{Fe}^{3+}\text{Al}^{3+}$ - $\text{Zn}^{2+}\text{Cu}^{2+}$, Fe^{3+} - $\text{Ni}^{2+}\text{Cu}^{2+}$ anionic clay, $\text{Al}^{3+}\text{Fe}^{3+}$ - Mg^{2+} anionic clay, $\text{Al}^{3+}\text{Fe}^{3+}$ - Zn^{2+} anionic clay, and Ru-doped Fe^{3+} - Zn^{2+} anionic clay.

Examples of anionic clays which fall under groups 1a and 1b both include Fe^{3+} - Fe^{2+} anionic clay, Fe^{3+} - $\text{Fe}^{2+}\text{Mg}^{2+}$ anionic clay, Fe^{3+} - $\text{Fe}^{2+}\text{Cu}^{2+}$ anionic clay, Fe^{3+} - $\text{Fe}^{2+}\text{Co}^{2+}$ anionic clay, Fe^{3+} - $\text{Fe}^{2+}\text{Zn}^{2+}$ anionic clay, $\text{Al}^{3+}\text{Fe}^{3+}$ - $\text{Fe}^{2+}\text{Cu}^{2+}$ anionic

clay, $\text{Al}^{3+}\text{Fe}^{3+}\text{-Fe}^{2+}\text{Co}^{2+}$ anionic clay, $\text{Al}^{3+}\text{Fe}^{3+}\text{-Fe}^{2+}\text{Zn}^{2+}$ anionic clay, $\text{Fe}^{3+}\text{-Fe}^{2+}\text{Cu}^{2+}\text{Zn}^{2+}$ anionic clay, $\text{Al}^{3+}\text{Fe}^{3+}\text{-Fe}^{2+}\text{Cu}^{2+}\text{Zn}^{2+}$ anionic clay.

Examples of iron-doped anionic clays (according to group 2) include iron-doped
 5 $\text{Al}^{3+}\text{-Mg}^{2+}$ anionic clay, iron-doped $\text{Al}^{3+}\text{-Zn}^{2+}$ anionic clay, iron-doped $\text{Ga}^{3+}\text{-Mg}^{2+}$
 anionic clay, iron-doped $\text{Al}^{3+}\text{-Ni}^{2+}$ anionic clay, iron-doped $\text{Al}^{3+}\text{-Co}^{2+}$ anionic
 clay, iron-doped $\text{Al}^{3+}\text{-Cu}^{2+}$ anionic clay, iron-doped $\text{Ga}^{3+}\text{-Mg}^{2+}$ anionic clay, iron-
 doped $\text{Cr}^{3+}\text{-Mg}^{2+}$ anionic clay, iron-doped $\text{La}^{3+}\text{-Mg}^{2+}$ anionic clay, iron-doped
 10 $\text{Ce}^{3+}\text{-Mg}^{2+}$ anionic clay, iron-doped $\text{Ga}^{3+}\text{-Zn}^{2+}$ anionic clay, iron-doped $\text{La}^{3+}\text{-Zn}^{2+}$
 anionic clay, iron-doped $\text{Ce}^{3+}\text{-Zn}^{2+}$ anionic clay, iron-doped $\text{Fe}^{3+}\text{-Fe}^{2+}$ anionic
 clay, iron-doped $\text{Fe}^{3+}\text{-M}^{2+}$ anionic clays (e.g. iron-doped $\text{Fe}^{3+}\text{-Mg}^{2+}$ anionic clay),
 and iron-doped $\text{M}^{3+}\text{-Fe}^{2+}$ anionic clays (e.g. iron-doped $\text{Al}^{3+}\text{-Fe}^{2+}$ anionic clay).

Preparation of anionic clays

15 Iron-containing anionic clays can be prepared by any method known in the art.
 For instance, a water-soluble iron(II) salt and a water-soluble trivalent metal salt
 (e.g. aluminium nitrate) can be co-precipitated from an aqueous solution,
 followed by aging of the precipitate to form an iron-containing anionic clay
 according to group 1a. Co-precipitation of a water-soluble iron(III) salt and a
 20 water-soluble divalent metal salt (e.g. magnesium nitrate) will result - after aging
 - in the formation of an iron-containing anionic clay according to group 1b.

It is also possible to age a slurry comprising a divalent iron compound and a
 trivalent metal compound, at least one of them being water-insoluble (by being
 in the form of, e.g., an oxide, hydroxide, carbonate, hydroxy carbonate, or oxy-
 25 hydroxide) to form an iron-containing anionic clay according to group 1a.
 Likewise, aging of a slurry comprising a trivalent iron compound and a divalent
 metal compound, at least one of them being water-insoluble, will result in an
 iron-containing anionic clay according to group 1b.

30 Iron-doped anionic clays according to group 2 can be prepared by impregnating
 an already formed anionic clay with an iron-containing compound, or by

preparing an anionic clay in the presence of an iron-containing compound. In the latter case, an iron-containing compound can be added to a slurry comprising a divalent and a trivalent metal compound which - after aging - form an anionic clay. It is also possible to prepare an iron-doped anionic clay by
5 aging a slurry comprising a divalent and a trivalent source, at least one of these sources being doped with an iron-containing compound.

If in the above methods for the preparation of iron-containing anionic clays according to groups 1 and 2 an excess of divalent and/or trivalent metal source
10 is used, compositions of iron-containing anionic clay and unreacted (meaning: not reacted to anionic clay) divalent and/or trivalent metal source - e.g. brucite, MgO, boehmite, iron (hydr)oxide and/or zinc (hydr)oxide - may be formed.

The iron-containing anionic clays according to groups 1 and 2 can be thermally
15 treated to form a solid solution, followed by rehydration to form an anionic clay again. This results in an increase in the physical strength of the particles. This thermal treatment and rehydration can also be applied to anionic clays before they are impregnated with an iron-containing compound to form an iron-doped anionic clay according to group 2.

20 Iron-containing anionic clays may be subjected to ion-exchange. Upon ion-exchange the interlayer charge-balancing anions are replaced with other anions. Examples of suitable anions are carbonate, bicarbonate, nitrate, chloride, sulphate, bisulphate, vanadates, tungstates, borates, phosphates, pillaring anions such as HVO_4^- , $\text{V}_2\text{O}_7^{4-}$, $\text{HV}_2\text{O}_{12}^{4-}$, $\text{V}_3\text{O}_9^{3-}$, $\text{V}_{10}\text{O}_{28}^{6-}$, $\text{Mo}_7\text{O}_{24}^{6-}$,
25 $\text{PW}_{12}\text{O}_{40}^{3-}$, $\text{B}(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, $[\text{B}_3\text{O}_3(\text{OH})_4]^-$, $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$, HBO_4^{2-} , HGao_3^{2-} , CrO_4^{2-} , and Keggin-ions, formate, acetate, and mixtures thereof.

Such an ion-exchange may also be applied to anionic clays before they are impregnated with iron-containing compound to form an iron-doped anionic clay
30 according to group 2.

Calcined iron-doped anionic clays according to group 3 are prepared by calcining an iron-doped anionic clay according to group 2, generally at temperatures in the range 200-1200°C under oxygen-containing or inert (e.g. N₂, Ar, He) atmosphere.

- 5 Calcined anionic clays according to group 4 are prepared by calcining an iron-containing anionic clay according to group 1a, generally at temperatures in the range 200-1200°C under oxygen-containing or inert (e.g. N₂, Ar, He) atmosphere.

10 Layered hydroxy salts

Metal hydroxy salts (LHS) are distinguished from anionic clays in that they are built up of divalent metals only, whereas layered double hydroxides are built up of both a divalent and a trivalent metal.

- 15 An example of a LHS is a hydroxy salt of a divalent metal according to the following idealised formula: $[(Me^{2+}, M^{2+})_2(OH)_3]^+(X^{n-})_{1/n}]$ wherein Me^{2+} and M^{2+} can be the same or different divalent metal ions and X is an anion other than OH⁻. Another example of LHS has the general formula $[(Me^{2+}, M^{2+})_5(OH)_8]^{2+}(X^{n-})_{2/n}]$ wherein Me^{2+} and M^{2+} can be the same or different divalent metal ions and X is an anion other than OH⁻.

- 20 If the LHS contains two different metals, the ratio of the relative amounts of the two metals may be close to 1. Alternatively, this ratio may be much higher, meaning that one of the metals predominates over the other. It is important to appreciate that these formulae are ideal and that in practice the overall structure will be maintained although chemical analysis may indicate compositions not
25 satisfying the ideal formula.

- The LHS-structures described above may be considered an alternating sequence of modified brucite-like layers in which the divalent metal(s) is/are coordinated octahedrally with hydroxide ions. In one family, structural hydroxyl
30 groups are partially replaced by other anions (e.g. nitrate) that may be

exchanged. In another family, vacancies in the octahedral layers are accompanied by tetrahedrally coordinated cations.

For further structural details as well as work on layered hydroxy salts the following publications are referenced:

- 5 *J. Solid State Chem.* 148 (1999) 26-40
Recent Res. Devel. In Mat. Sci. 1 (1998) 137-188
Solid State Ionics 53-56 (1992) 527-533
Inorg. Chem. 32 (1993) 1209-1215
J. Mater. Chem. 1 (1991) 531-537
- 10 *Russian J Inorganic Chemistry*, 30, (1985) 1718-1720
Reactivity of Solids, 1, (1986) 319-327
Reactivity of Solids, 3, (1987) 67-74
Compt. Rend. 248, (1959) 3170-3172
- 15 Layered hydroxy salts in which iron is a divalent metal (according to group 1a) include Fe-LHS, Fe-Co LHS, Zn-Fe LHS, Fe-Co LHS, Zn-Fe-Co LHS, Mg-Fe-Co LHS, and Zn-Cu-Fe LHS. It will be clear from their definition that layered hydroxy salts according to group 1b do not exist.
Examples of iron-doped layered hydroxy salts (according to group 2) include
20 iron-doped Zn-LHS (e.g. $\text{Zn}_5(\text{OH})_8(\text{X})_2$, $\text{Zn}_4(\text{OH})_6\text{X}$), iron-doped Cu-LHS (e.g. $\text{Cu}_2(\text{OH})_3\text{X}$, $\text{Cu}_4(\text{OH})_6\text{X}$, $\text{Cu}_7(\text{OH})_{12}(\text{X})_2$), iron-doped Co-LHS (e.g. $\text{Co}_2(\text{OH})_3\text{X}$, iron-doped Ni-LHS (e.g. $\text{Ni}_2(\text{OH})_3\text{X}$), iron-doped Mg-LHS (e.g. $\text{Mg}_2(\text{OH})_3\text{X}$), iron-doped Mn-LHS, iron-doped Zn-Cu LHS, iron-doped Zn-Ni LHS, iron-doped Zn-Co LHS, iron-doped Zn-Mn LHS, iron-doped Ni-Cu LHS, iron-doped Cu-Co
25 LHS, iron-doped Cu-Mg LHS, iron-doped Cu-Mn LHS, iron-doped Ni-Co LHS, iron-doped Ni-Cu-Co LHS, iron-doped Fe-LHS, iron-doped Fe-Co LHS, iron-doped Zn-Fe LHS, iron-doped Fe-Co LHS, iron-doped Zn-Fe-Co LHS, iron-doped Mg-Fe-Co LHS, and iron-doped Zn-Cu-Fe LHS.
- 30 The iron-containing LHS may contain additives other than iron, such as rare earth metals (e.g. Ce, La), Al, Si, P, B, group VI, group VIII, alkaline earth (for

instance Ca and Ba) and/or transition metals (for example Mn, Ti, Zr, Cu, Ru, Co, Ni, Zn, Mo, V, W, Sn). The use of Al as additive is advantageous for creating porosity in the LHS structure. La, B, Si, and Mg can improve the sinter resistance of the LHS.

- 5 Examples of iron-containing LHS containing additives other than iron include Fe-LHS doped with 4-6 wt% Zn (calculated as ZnO) and Fe-LHS doped with 2-3 wt% Zn (calculated as ZnO) and 3-4 wt% Cu (calculated as CuO).

Examples of suitable interlayer anions X^{n-} are the inorganic anions NO_3^- , NO_2^- , CO_3^{2-} , HCO_2^- , SO_4^{2-} , SO_3NH_2 , $\text{P}_2\text{O}_7^{2-}$, MnO_4^- , SCN^- , $\text{S}_2\text{O}_6^{2-}$, $\text{Si}_8\text{O}_{20}^{8-}$, SeO_4^- , F^- , Cl^- , Br^- , I^- , ClO_3^- , ClO_4^- , BrO_3^- , and IO_3^- and the organic anions acetate, long chain carboxylates (e.g. sebacate, caprate and caprylate (CPL)), alkylsulfates (e.g. dodecylsulfate (DS) and dodecylbenzenesulfate), benzoate, and phthalocyanine tetrasulfonate. Exchange of these ions has been fully
 10 documented in the literature. By controlling the exchange conditions mixed inorganic/organic compositions can be obtained e.g. $\text{Cu}_2(\text{OH})_3(\text{NO}_3)(\text{CPL})_{0.2}(\text{DS})_{0.5}(\text{H}_2\text{O})_{0.1}$.

LHS exchanged with (bi)carbonates or organic anions provides the advantage that upon calcination, the anion will decompose, thereby increasing the porosity
 15 and surface area of the LHS

Preparation of layered hydroxy salts

Suitable methods for the preparation of layered hydroxy salts involve the reaction of a metal oxide with a dissolved metal salt (see *Inorg. Chem.* 32
 25 (1993) 1209-1215) and (co-)precipitation from metal salt solutions (see *J. Solid State Chem.* 148 (1999) 26-40 and *J. Mater. Chem.* 1 (1991) 531-537). After preparation of the LHS, the interlayer anions may be exchanged, if so desired, by a regular ion-exchange procedure.

30 So, according to these methods, iron-containing LHS according to group 1a can be prepared by reacting (i) an iron oxide with a dissolved divalent metal salt

(either a Fe(II) salt or another divalent metal salt), (ii) a Fe(II) salt with a divalent metal oxide, or (iii) by co-precipitating a Fe(II) salt with another divalent metal salt.

5 Iron-doped LHS according to group 2 can be prepared by impregnating an existing LHS, reacting a divalent metal salt with another divalent metal salt or divalent metal oxide in the presence of an iron compound, or by using an iron-doped divalent metal oxide for the preparation of a LHS.

10 Calcined iron-doped layered hydroxy salts according to group 3 are prepared by calcining an iron-doped layered hydroxy salts according to group 2, generally at temperatures in the range 200-1200°C under oxygen-containing or inert (e.g. N₂, Ar, He) atmosphere.

Calcined layered hydroxy salts according to group 4 are prepared by calcining
15 an iron-containing layered hydroxy salt according to group 1a, generally at temperatures in the range 200-1200°C under oxygen-containing or inert (e.g. N₂, Ar, He) atmosphere.

Cationic clays

20 Cationic clays differ from anionic clays in that they have a crystal structure consisting of negatively charged layers built up of specific combinations of tetravalent, trivalent, and optionally divalent metal hydroxides between which there are cations and water molecules.

Suitable iron-containing cationic clays for use in the present invention include
25 natural and synthetic iron-containing cationic clays.

Iron-containing cationic clays according to group 1 include iron-containing smectites, iron-containing illites, iron-containing micas, iron-containing glauconites, iron-containing attapulgite, etc.

Iron-doped cationic clays (according to group 2) are generally prepared by exchanging a cationic clay with Fe^{2+} , Fe^{3+} , or cationic iron-containing complexes. Alternatively, they are impregnated with an iron compound, or the iron compound is present during preparation of the cationic clay.

- 5 Examples of suitable cationic clays to be impregnated or ion-exchanged with an iron-containing compound are smectites (including montmorillonite, beidellite, nontronite, hectorite, saponite, laponiteTM, and sauconite), bentonite, illites, micas, glauconite, vermiculites, attapulgite, and sepiolite.
- 10 Calcined iron-doped cationic clays according to group 3 are prepared by calcining an iron-doped cationic clay according to group 2, generally at temperatures in the range 200-1200°C under oxygen-containing or inert (e.g. N_2 , Ar, He) atmosphere.
- Calcined cationic clays according to group 4 are prepared by calcining an iron-
- 15 containing cationic clay according to group 1a, generally at temperatures in the range 200-1200°C under oxygen-containing or inert (e.g. N_2 , Ar, He) atmosphere.

Cationic layered materials

- 20 Cationic Layered Materials (CLMs) are crystalline $\text{NH}_4\text{-Me(II)-TM-O}$ phases with a characteristic X-ray diffraction pattern. In this structure, Me(II) represents a divalent metal and TM stands for a transition metal. The structure of a CLM consists of negatively charged layers of divalent metal octahedra and transition metal tetrahedra with charge-compensating cations sandwiched between these
- 25 layers.

- Iron-containing CLMs according to group 1 have Fe(II) as the divalent metal. Hence, they belong to group 1a. One of the methods by which they can be prepared is the one according to M.P. Astier et al. (*Ann. Chim. Fr.* Vol. 12,
- 30 1987, pp. 337-343), which involves the reaction of an ammonium transition metal salt (e.g. ammonium heptamolybdate) and a Fe(II) salt in aqueous

ammonia solution. Upon evaporation of ammonia a precipitate is formed, which is then aged to form a CLM.

Another method is that according to D. Levin, S. Soled, and J. Ying (*Chem. Mater.* Vol. 8, 1996, 836-843; *ACS Symp. Ser.* Vol. 622, 1996, 237-249; *Stud. Surf, Sci. Catal.* Vol. 118, 1998, 359-367). This method involves the steps of (a) precipitating a Fe(II) salt and aluminium nitrate, (b) aging the precipitate to form an anionic clay, (c) calcining the anionic clay to form a mixed oxide, and (d) contacting and reacting the mixed oxide with ammonium transition metal salts (e.g. ammonium heptamolybdate) to form a CLM.

10 A third method is that according to non-published patent application no. PT/EP03/06646, which involves the steps of (a) preparing a slurry comprising a water-insoluble aluminium source and a Fe(II) source, (b) drying the slurry of step a) and calcining the dried material to form a first calcined material, (c) optionally rehydrating the product of step b) to obtain an anionic clay, followed
15 by calcining the anionic clay to form a second calcined material, (d) contacting a slurry of either the first or the second calcined material with an ammonium transition metal salt, and (e) aging the resulting slurry.

Iron-doped CLMs according to group 2 can be prepared by impregnating a CLM
20 with an iron-containing compound or by preparing the CLM in the presence of an iron-containing compound.

Other additives can be present in or on the CLM. Such additives include compounds of rare earth metals (e.g. Ce, La), Si, P, B, group VI metals, group
25 VIII metals, alkaline earth (for instance Ca, Mg, and Ba) and/or transition metals (for example Mn, Ti, Zr, Cu, Ru, Co, Ni, Zn, Mo, V, W, Sn).

Calcined iron-doped CLMs according to group 3 are prepared by calcining an iron-doped CLM according to group 2, generally at temperatures in the range
30 200-1200°C under oxygen-containing or inert (e.g. N₂, Ar, He) atmosphere.

Calcined CLMs according to group 4 are prepared by calcining an iron-containing CLM according to group 1a, generally at temperatures in the range 200-1200°C under oxygen-containing or inert (e.g. N₂, Ar, He) atmosphere.

5 Catalyst compositions

The Fischer-Tropsch catalyst precursor used in the process according to the invention can consist solely of one or more iron-containing layered material(s). However, it can be advantageous to have other catalyst components present, such as iron-free anionic clays, e.g. Al-Mg anionic clay, magnesium (hydr)oxide,
10 iron hydroxide, e.g. Fe(OH)₃ or FeOOH, iron oxide, alumina, titania, silica, and/or zinc (hydr)oxide.

Furthermore, it is possible to add additives to the Fischer-Tropsch catalyst precursor, either by having one or more additives present during preparation of
15 the iron-containing layered material, or by impregnating the iron-containing layered material with one or more additives. Suitable additives are compounds of rare earth metals (e.g. Ce, La), Si, P, B, group VI metals, group VIII noble metals (Pt, Pd), alkaline earth (for instance Ca, Mg, and Ba), alkaline metals (e.g. K) and/or transition metals (for example Mn, Ti, Zr, Cu, Ru, Co, Ni, Zn, Mo,
20 V, W, Sn, Cr, Re, Rh).

The Fischer-Tropsch synthesis

Before use in the Fischer-Tropsch synthesis, the Fischer-Tropsch catalyst precursor may be reduced - according to step b) of the method according to the
25 invention - to form the Fischer-Tropsch catalyst. This reduction can be performed either *in situ* or *ex situ* and preferably in a hydrogen-containing atmosphere at temperatures in the range 200-600°C.

If no reduction step is performed, the final Fischer-Tropsch catalyst will be formed from the Fischer-Tropsch catalyst precursor during Fischer-Tropsch
30 synthesis.

The Fischer-Tropsch synthesis - according to step c) of the method according to the invention - can be conducted in any manner known in the art for performing this reaction over iron-containing catalysts. Typically, it is conducted at temperatures between 200 and 400°C and pressures between about 1 and 70 atm, preferably 1-30 atm, in a slurry reactor, a fixed bed reactor, or a fluidized bed reactor. Typical H₂/CO ratios range from 0.5 to 6.0, more preferably 0.5-2.0.

EXAMPLES

10

Example 1

An aqueous solution of Fe(NO₃)₃·9H₂O (0.17 mol) and Mg(NO₃)₂·6H₂O (0.51 mol) was added slowly to an aqueous solution of KOH and K₂CO₃. After two hours of stirring, the solution was brought to pH=9.5. The precipitate was aged for 16 hours at 70°C and subsequently isolated, washed with de-ionized water, and dried at 85°C. XRD and chemical analysis revealed the quantitative formation of a Fe³⁺-Mg²⁺ anionic clay according to group 1b.

Example 2

20 An aqueous solution of Mg(NO₃)₂·6H₂O (0.24 mol), Al(NO₃)₃·9H₂O (0.10 mol), and FeSO₄·7H₂O (0.06 mol) was added slowly to 200 mL de-ionized water under N₂-atmosphere. Simultaneously, an aqueous solution of Na₂CO₃ (1M) was added. During the addition of the two aqueous solutions, the reaction medium was kept at 40°C and pH=8.5. The resulting precipitate was aged for 24 hours at 40°C under stirring. The product was washed with de-ionized water and dried at 85°C. XRD and chemical analysis revealed the quantitative formation of an Al³⁺-Mg²⁺-Fe²⁺ anionic clay according to group 1a.

Example 3

The product of Example 2 was calcined in air at 350°C for 5 hours to obtain a calcined Fe-containing anionic clay according to group 4.

5 Example 4

An aqueous solution of $\text{Fe}(\text{NO}_3)_3$ (0.25 mol) in de-ionized water was added slowly to a suspension of MgO (0.53 mol) and $\text{Mg}(\text{OH})_x(\text{CO}_3)_y$ (0.23 mol) in de-ionized water. The reaction mixture was brought to pH=9.5 and subsequently stirred at 80°C for 16 hours. The precipitate was isolated by filtration, washed
10 with de-ionized water, and dried at 85°C. XRD and chemical analysis revealed the quantitative formation of a Fe^{3+} - Mg^{2+} anionic clay according to group 1b.

Example 5

A suspension of $\text{Fe}(\text{OH})_3$ (0.25 mol) in de-ionized water was added to a
15 suspension of MgO (0.53 mol) and $\text{Mg}(\text{OH})_x(\text{CO}_3)_y$ (0.23 mol) in de-ionized water. The reaction mixture was aged at 80°C for 24 hours under stirring. The precipitate was isolated by filtration and dried at 85°C. XRD and chemical analysis revealed the quantitative formation of a Fe^{3+} - Mg^{2+} anionic clay according to group 1b.

20

Example 6

A suspension of $\text{Fe}(\text{OH})_3$ (0.25 mol) in de-ionized water was added to a suspension of MgO (0.53 mol) and $\text{Mg}(\text{OH})_x(\text{CO}_3)_y$ (0.23 mol) in de-ionized water. The reaction mixture was aged at 140°C under hydrothermal conditions
25 for 24 hours under stirring. The precipitate was isolated by filtration and dried at 85°C. XRD revealed the formation of a Fe^{3+} - Mg^{2+} anionic clay according to group 1b.

Example 7

An aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1 mol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3 mol) was added slowly to an aqueous solution of $(\text{NH}_4)_2\text{CO}_3$. The pH of the solution was kept at 7 by introducing NaOH. The precipitate was aged for 1 hour at room temperature and subsequently isolated, washed with de-ionized water, and dried at 120°C. XRD and chemical analysis revealed the quantitative formation of a Fe^{3+} - Zn^{2+} anionic clay according to group 1b.

Example 8

10 An aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1 mol) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3 mol) was added slowly to an aqueous solution of Na_2CO_3 at 65 °C. The pH of the solution was kept at 10 by introducing NaOH. The precipitate was aged for 1 hour at 65°C and subsequently isolated, washed with de-ionized water, and dried at 120°C. XRD and chemical analysis revealed the quantitative formation of a
15 Fe^{3+} - Co^{2+} anionic clay according to group 1b.

Example 9

In a 10-litre autoclave MgO (ex Nedmag ®) and Bauxite Ore Concentrate (BOC) were slurried in water in a ratio of 4 to 1. The slurry was milled and
20 hydrothermally treated at 170°C for 90 minutes. The XRD pattern of the product – after drying at 120°C - showed the presence of 3R_2 -type anionic clay according to WO 01/12550.

The anionic clay was impregnated with an aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ using an appropriate liquid volume for incipient wetness impregnation (c 0.6-0.8
25 mL/g) and an iron concentration leading to an iron loading of 10 wt% (calculated as Fe_2O_3 and based on total weight of doped anionic clay). The impregnated anionic clay was dried in air at 120°C for three hours, resulting in an anionic clay doped with 10 wt% Fe (calculated as Fe_2O_3 and based on the total weight of the doped anionic clay) according to group 2.

Example 10

The product of Example 9 was calcined in air at 350°C for 5 hours to obtain a calcined Fe-doped anionic clay according to group 3.

5 Example 11

The iron-containing anionic clays according to Examples 1-10 were tested for their Fischer-Tropsch activity, selectivity, and stability in a fixed bed reactor at atmospheric pressure using two different tests.

For comparison, the same tests were applied to two types of reference
10 materials: (i) "state of the art" iron oxide catalysts (prepared by a precipitation reaction between iron salts and a base) and (ii) a mixed metal oxide containing both magnesium oxide and iron oxide (atomic ratio Mg:Fe = 3:1) prepared by co-precipitation of a mixture of magnesium salts and iron salts with a base.

15 The first test involved pulse-testing of an accurately defined amount of CO in a flow of H₂ during a well-defined time-span, applying the apparatus described in International Patent Application No. WO 01/79835, page 7, line 24 through page 8, line 3 for pulse-chemisorption.

A catalyst sample (200 mg) was first reduced under flowing H₂ (total flow 20
20 mL/min) while increasing the temperature from room temperature to 400°C with a ramp of 10°C/min. The sample was subsequently kept at 400°C for 4 hours under H₂-flow (total flow 20mL/min). Next, the sample was allowed to cool down to room temperature while flowing He. CO pulse-testing was performed at room temperature and measured with a TCD (total flow He=16 mL/min, 8 µL CO per
25 pulse). Then, the samples were treated by flowing H₂ (total flow 20 mL/min) and increasing the temperature from room temperature to 400°C with a ramp of 10°C/min. The samples were kept at 400°C for 30 minutes under flowing H₂ (total flow 20 mL/min) and subsequently allowed to cool down to 250°C in H₂-atmosphere. The Fischer-Tropsch activity was measured by measuring the
30 response of small CO pulses in a H₂-flow (total H₂ flow =20 mL/min, 8 µL CO

per pulse) at 250°C using a FID. After stripping the surface of the samples with H₂, this activity test was repeated.

The second test was conducted in a micro-flow apparatus. The samples were
5 diluted with SiC, placed the reactor tube, and pre-treated in a mixture of 10
vol.% H₂ in He (total flow 100 mL/min) at a temperature increasing from room
temperature to 400°C at a rate of 1°C/min. This temperature was maintained for
9 hours. Prior to the start of the reaction the samples were cooled to 300°C. The
reactor feed consisted of a flow of 30 mL/min of a mixture of H₂ and CO (H₂/CO
10 ratio = 2). The hydrocarbons in the effluent were measured online by a GC-17
Shimadzu gas chromatograph (Al₂O₃/KCl), while CO and CO₂ were measured
offline on a Varian gas chromatograph (Poraplot U/Molsieve 5A).

Activity

- 15 The first test showed that the Fischer-Tropsch activity – per gram of iron - of the
samples according to Examples 1-10 was a factor 2-6 larger than that of the
most active iron oxide reference material. The activity of the mixed oxide
reference material was even lower than that of the iron oxide reference
materials.
- 20 The second test showed that - at 2 hours running time - the Fischer-Tropsch
activity – per gram of iron - of the samples according to Examples 1-10 was a
factor 10-30 larger than that of the most active iron oxide reference material.
The activity of the mixed oxide reference material was even lower than that of
the iron oxide reference materials.
- 25 It was also found that the activity of the product of Example 3 was somewhat
higher than that of its uncalcined version of Example 2.

Stability

- Furthermore, the activity of the samples according to Examples 1-10 was stable
30 from 1 hour (steady-state) to 6 hours running time, while the activity of the iron

oxide reference materials gradually decreased by a factor 2-3 in this time period.

Selectivity

- 5 Except for the sample according to Example 7, all iron-containing anionic clays showed a lower selectivity towards methane than the iron oxide and the mixed oxide reference materials. Furthermore, the selectivity towards methane of the iron oxide reference materials increased by a factor 1.4-1.7 during the test run, while for the iron-containing anionic clays the selectivity towards methane
- 10 remained constant.

CLAIMS

1. Method for performing a Fischer-Tropsch process comprising the steps of:
 - a) selecting a Fischer-Tropsch catalyst precursor,
 - 5 b) optionally reducing the Fischer-Tropsch catalyst precursor to form a Fischer-Tropsch catalyst, and
 - c) performing a Fischer-Tropsch synthesis using the Fischer-Tropsch catalyst precursor according to step a) or the Fischer-Tropsch catalyst according to step b),
- 10 wherein the Fischer-Tropsch catalyst precursor comprises an iron-containing layered material selected from the group consisting of layered materials in which iron is present in the layered structure as divalent and/or trivalent metal (group 1), iron-doped layered materials (group 2), calcined iron-doped layered materials (group 3), and calcined layered materials in
15 which iron is present in the layered structure as divalent metal (group 4).
2. A method according to claim 1 wherein the Fischer-Tropsch catalyst precursor comprises an iron-doped layered material (group 2) or a calcined iron-doped layered material (group 3).
- 20 3. A method according to claim 2 wherein the iron-doped layered material is an iron-doped anionic clay.
4. A method according to claim 2 wherein the iron-doped layered material is
25 an iron-doped layered hydroxy salt.
5. A method according to claim 2 wherein the iron-doped layered material is an iron-doped cationic layered material.

6. Fischer-Tropsch process according to any one of claims 2-5 wherein the iron-doped layered material contains 1-35 wt% of iron calculated as Fe_2O_3 and based on the weight of the iron-doped layered material.
- 5 7. Fischer-Tropsch process according to claim 1 wherein the Fischer-Tropsch catalyst precursor comprises a layered material in which iron is present in the layered structure as divalent metal (group 1a) or a calcined layered material in which iron is present in the layered structure as divalent metal (group 4).
- 10 8. Fischer-Tropsch process according to claim 1 wherein the Fischer-Tropsch catalyst precursor comprises a layered material in which iron is present in the layered structure as trivalent metal (group 1b).
- 15 9. Fischer-Tropsch process according to claim 7 or 8 wherein the layered material is an anionic clay.
10. Fischer-Tropsch process according to claim 7 wherein the layered material is a layered hydroxy salt.
- 20 11. Fischer-Tropsch process according to claim 7 wherein the layered material is a cationic layered material.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/08770

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 B01J23/745 C07C1/04 C10G2/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 B01J C07C C10G		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SHEN J, GUANG B, TU M, CHEN Y: "Pepraration and characterization of Fe/MgO catalysts obtained from hydrotalcite-like compounds" CATALYSIS TODAY, vol. 30, 1996, page 77-82 XP002265886 cited in the application cf. "1.Introduction" (last three lines) and "2.Experimental" (right hand column) <div style="text-align: center;">--- -/-</div>	1-11
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div>		
* Special categories of cited documents :		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*&* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center;">22 December 2003</div>		Date of mailing of the international search report <div style="text-align: center;">13/01/2004</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center;">Gosselin, D</div>

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/08770

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	TU M, SHEN J, CHEN Y: "Microcalorimetric studies of surface acid/base properties of magnesium-iron catalysts prepared from hydrotalcite-type precursors" JOURNAL OF SOLID STATE CHEMISTRY, vol. 128, 1997, page 73-79 XP002265887 cited in the application cf. Introduction, last paragraph, reference 24	1-11
X	US 4 665 044 A (TZOU MING S ET AL) 12 May 1987 (1987-05-12) abstract column 1, line 10 - line 20 column 2, line 62 -column 3, line 14 column 3, line 34 - line 36 claims; examples I,XXXI	1-11
X	US 4 920 086 A (RAYTHATHA RASIK H ET AL) 24 April 1990 (1990-04-24) column 1, line 8 - line 23 column 3, line 41 - line 68 claims; examples	1-11
X	US 2 850 515 A (MCGRATH HENRY G ET AL) 2 September 1958 (1958-09-02) column 1, line 15 - line 18 column 1, line 36 - line 38 column 3, line 37 -column 4, line 52 column 6, line 19 -column 8, line 24 column 10, line 65 -column 12, line 29 claims 1-3,9-11,13 cf. iron-comprising catalysts in the table of column 11	1-11
A	US 4 559 363 A (HENSLEY JR ALBERT L ET AL) 17 December 1985 (1985-12-17) column 4, line 18 - line 21 column 4, line 45 - line 48 column 5, line 18 - line 23 column 7, line 33 - line 58 column 8, line 39 - line 43 column 10, line 22 - line 58 column 12, line 34 -column 14, line 18 examples 5,9 claims	1-11
P,A	WO 02 089978 A (SUD CHEMIE INC) 14 November 2002 (2002-11-14) claims 1,8,11,12	1-11

-/--

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/08770

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>HEREIN D ET AL: "On the nature of the so-called iron-graphite" CARBON, ELSEVIER SCIENCE PUBLISHING, NEW YORK, NY, US, vol. 35, no. 1, 1997, pages 17-29, XP004016637 ISSN: 0008-6223 page 17, right-hand column, line 1-3 -----</p>	1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/08770

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4665044	A	12-05-1987	US 4629712 A US 4665045 A	16-12-1986 12-05-1987
US 4920086	A	24-04-1990	AU 2082388 A NZ 225212 A WO 8900083 A1 US 4855268 A	30-01-1989 28-08-1990 12-01-1989 08-08-1989
US 2850515	A	02-09-1958	NONE	
US 4559363	A	17-12-1985	NONE	
WO 02089978	A	14-11-2002	WO 02089978 A1	14-11-2002